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TITLE: Fuel Cells Comprising Laminar Flow
Induced Dynamic Conducting
Interfaces, Electronic Devices
Comprising Such Cells, and Methods
Employing Same

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FUEL CELLS COMPRISING LAMINAR FLOW INDUCED DYNAMIC CONDUCTING INTERFACES, ELECTRONIC DEVICES COMPRISING SUCH CELLS, AND METHODS EMPLOYING SAME

CROSS-REFERENCES TO RELATED APPLICATIONS

5   The present application is a continuation-in-part of application No. 10/053,187, filed on January 14, 2002, titled "Electrochemical cells comprising laminar flow induced dynamic conducting interfaces, electronic devices comprising such cells, and methods employing same", inventors Larry J. Markoski et al., hereby incorporated by reference in its entirety.

BACKGROUND

10   This invention relates to the field of induced dynamic conducting interfaces. More particularly, this invention relates to laminar flow induced dynamic conducting interfaces for use in micro-fluidic batteries, fuel cells, and photoelectric cells.

15   A key component in many electrochemical cells is a semi-permeable membrane or salt bridge. One of the primary functions of these components is to physically isolate solutions or solids having different chemical potentials. For example, fuel cells generally contain a semi-permeable membrane (e.g., a polymer electrolyte membrane or PEM) that physically isolates the anode and

20   cathode regions while allowing ions (e.g., hydrogen ions) to pass through the membrane. Unlike the ions, however, electrons generated at the anode cannot pass through this membrane, but instead travel around it by means of an external circuit. Typically, semi-permeable membranes are polymeric in nature and have finite life cycles due to their inherent chemical and thermal

25   instabilities. Moreover, such membranes typically exhibit relatively poor mechanical properties at high temperatures and pressures, which seriously limits their range of use.

        Fuel cell technology shows great promise as an alternative energy source for numerous applications. Several types of fuel cells have been

30   constructed, including: polymer electrolyte membrane fuel cells, direct

methanol fuel cells, alkaline fuel cells, phosphoric acid fuel cells, molten carbonate fuel cells, and solid oxide fuel cells. For a comparison of several fuel cell technologies, see Los Alamos National Laboratory monograph LA-UR-99-3231 entitled *Fuel Cells: Green Power* by Sharon Thomas and Marcia Zalbowitz, the entire contents of which are incorporated herein by reference, except that in the event of any inconsistent disclosure or definition from the present application, the disclosure or definition herein shall be deemed to prevail.
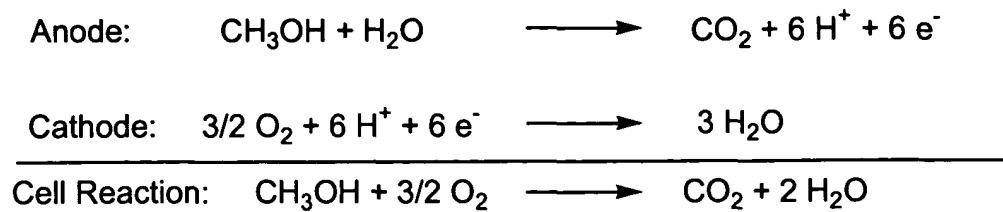
Although all fuel cells operate under similar principles, the physical components, chemistries, and operating temperatures of the cells vary greatly. For example, operating temperatures can vary from room temperature to about 1000 °C. In mobile applications (for example, vehicular and/or portable microelectronic power sources), a fast-starting, low weight, and low cost fuel cell capable of high power density is required. To date, polymer electrolyte fuel cells (PEFCs) have been the system of choice for such applications because of their low operating temperatures (e.g., 60-120 °C), and inherent ability for fast start-ups.

FIG. 1 shows a cross-sectional schematic illustration of a polymer electrolyte fuel cell **2**. PEFC **2** includes a high surface area anode **4** that acts as a conductor, an anode catalyst **6** (typically platinum alloy), a high surface area cathode **8** that acts as a conductor, a cathode catalyst **10** (typically platinum), and a polymer electrolyte membrane (PEM) **12** that serves as a solid electrolyte for the cell. The PEM **12** physically separates anode **4** and cathode **8**. Fuel in the gas and/or liquid phase (typically hydrogen or an alcohol) is brought over the anode catalyst **6** where it is oxidized to produce protons and electrons in the case of hydrogen fuel, and protons, electrons, and carbon dioxide in the case of an alcohol fuel. The electrons flow through an external circuit **16** to the cathode **8** where air, oxygen, or an aqueous oxidant (e.g., peroxide) is being constantly fed. Protons produced at the anode **4** selectively diffuse through PEM **12** to cathode **8**, where oxygen is reduced in the presence of protons and electrons at cathode catalyst **10** to produce water.
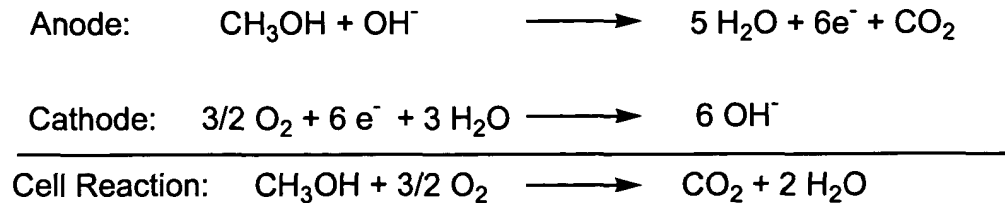
The PEM used in conventional PEFCs is typically composed of a perfluorinated polymer with sulphonic acid pendant groups, such as the material sold under the tradename NAFION by DuPont (Fayetteville, NC) (see: *Fuel Cell Handbook, Fifth Edition* by J. Hirschenhofer, D. Stauffer, R. Engleman, and M. Klett, **2000**, Department of Energy—FETL, Morgantown, WV; and L. Carrette, K. A. Friedrich, and U. Stimming in *Fuel Cells*, **2001**, *1*(1), 5). The PEM serves as catalyst support material, proton conductive layer, and physical barrier to limit mixing between the fuel and oxidant streams. Mixing of the two feeds would result in direct electron transfer and loss of efficiency since a mixed potential and/or thermal energy is generated as opposed to the desired electrical energy.

Operating the cells at low temperature does not always prove advantageous. For example, carbon monoxide (CO), which may be present as an impurity in the fuel or as the incomplete oxidation product of an alcohol, binds strongly to and "poisons" the platinum catalyst at temperatures below about 150 °C. Therefore, CO levels in the fuel stream must be kept low or removed, or the fuel must be completely oxidized to carbon dioxide at the anode. Strategies have been employed either to remove the impurities (e.g., by an additional purification step) or to create CO-tolerant electrodes (e.g., platinum alloys). In view of the difficulties in safely storing and transporting hydrogen gas, the lower energy density per volume of hydrogen gas as compared to liquid-phase fuels, and the technological advances that have occurred in preparing CO-tolerant anodes, liquid fuels have become the phase of choice for mobile power sources.

Numerous liquid fuels are available. Notwithstanding, methanol has emerged as being of particular importance for use in fuel cell applications. FIG. 2 shows a cross-sectional schematic illustration of a direct methanol fuel cell (DMFC) **18**. The electrochemical half reactions for a DMFC are as follows in acidic conditions:

$$\text{Anode:} \quad CH_3OH + H_2O \quad \longrightarrow \quad CO_2 + 6\,H^+ + 6\,e^-$$

$$\text{Cathode:} \quad 3/2\,O_2 + 6\,H^+ + 6\,e^- \quad \longrightarrow \quad 3\,H_2O$$

$$\text{Cell Reaction:} \quad CH_3OH + 3/2\,O_2 \quad \longrightarrow \quad CO_2 + 2\,H_2O$$

whereas in alkaline conditions the half reactions are:

$$\text{Anode:} \quad CH_3OH + OH^- \quad \longrightarrow \quad 5\,H_2O + 6e^- + CO_2$$

$$\text{Cathode:} \quad 3/2\,O_2 + 6\,e^- + 3\,H_2O \quad \longrightarrow \quad 6\,OH^-$$

$$\text{Cell Reaction:} \quad CH_3OH + 3/2\,O_2 \quad \longrightarrow \quad CO_2 + 2\,H_2O$$

5   As shown in FIG. 2, the cell utilizes methanol fuel directly, and does not require a preliminary reformation step. DMFCs are of increasing interest for producing electrical energy in mobile power (low energy) applications. However, at present, several fundamental limitations have impeded the

10   development and commercialization of DMFCs.

One of the major problems associated with DMFCs is that the semi-permeable membrane used to separate the fuel feed (i.e., methanol) from the oxidant feed (i.e., oxygen) is typically a polymer electrolyte membrane (PEM) of the type developed for use with gaseous hydrogen fuel feeds. These

15   PEMs, in general, are not fully impermeable to methanol. As a result, an undesirable occurrence known as "methanol crossover" takes place, whereby methanol travels from the anode to the cathode through the membrane. In addition to being an inherent waste of fuel, methanol crossover also causes depolarization losses (mixed potential) at the cathode and, in general, leads to

20   decreased cell performance.

Therefore, in order to fully realize the promising potential of DMFCs as commercially viable portable power sources, the problem of methanol crossover must be addressed. Moreover, other improvements are also needed including: increased cell efficiency, reduced manufacturing costs,

25   increased cell lifetime, and reduced cell size/weight. In spite of massive

research efforts, these problems persist and continue to inhibit the commercialization and development of DMFC technology.

A considerable amount of research has already been directed at solving the aforementioned problem of methanol crossover. Solutions have typically centered on attempts to increase the rate of methanol consumption at the anode, and attempts to decrease the rate of methanol diffusion to the cathode (see: A. Heinzel, and V. M. Barragan in *J. Power Sources*, **1999**, *84*, 70, and references therein). Strategies for increasing the rate of methanol consumption at the anode have included increasing catalyst loading (i.e., providing a larger surface area), increasing catalyst activity (i.e., increasing efficiency), and raising operating pressure and/or temperature. Strategies for decreasing the rate of methanol diffusion to the cathode have included decreasing methanol concentrations, fabricating thicker NAFION membranes, synthesizing new proton conducting materials having low permeability to methanol, lowering cell operating temperature, and fabricating methanol tolerant cathodes. However, to date, there remain pressing needs in DMFC technology for significantly lowered fabrication costs, increased efficiency, extended cell lifetimes, and appreciably reduced cell sizes/weights.

SUMMARY

The scope of the present invention is defined solely by the appended claims, and is not affected to any degree by the statements within this summary.

In a first aspect, the present invention provides a fuel cell that includes (a) a first electrode; (b) a second electrode; and (c) a channel contiguous with at least a portion of the first and the second electrodes; such that when a first liquid is contacted with the first electrode, a second liquid is contacted with the second electrode, and the first and the second liquids flow through the channel, a multistream laminar flow is established between the first and the second liquids, and a current density of at least 0.1 mA/cm^2 is produced.

In a second aspect, the present invention provides a device that includes a fuel cell as described above.

In a third aspect, the present invention provides a portable electronic device that includes a fuel cell as described above.

In a fourth aspect, the present invention provides a method of generating an electric current that includes operating a fuel cell as described above.

In a fifth aspect, the present invention provides a method of generating water that includes operating a fuel cell as described above.

In a sixth aspect, the present invention provides a method of generating electricity that includes flowing a first liquid and a second liquid through a channel in multistream laminar flow, wherein the first liquid is in contact with a first electrode and the second liquid is in contact with a second electrode, wherein complementary half cell reactions take place at the first and the second electrodes, respectively, and wherein a current density of at least 0.1 mA/cm^2 is produced.

In a seventh aspect, the present invention provides a fuel cell that includes a first electrode and a second electrode, wherein ions travel from the first electrode to the second electrode without traversing a membrane, and wherein a current density of at least 0.1 mA/cm^2 is produced.

In an eighth aspect, the present invention provides the improvement comprising replacing the membrane separating a first and a second electrode of a fuel cell with a multistream laminar flow of a first liquid containing a fuel in contact with the first electrode, and a second liquid containing an oxidant in contact with the second electrode, and providing each of the first liquid and the second liquid with a common electrolyte.

In a ninth aspect, the present invention provides a fuel cell that includes (a) a support having a surface; (b) a first electrode connected to the surface of the support; (c) a second electrode connected to the surface of the support and electrically coupled to the first electrode; (d) a spacer connected to the surface of the support, which spacer forms a partial enclosure around at least a portion of the first and the second electrodes; and (e) a microchannel contiguous with at least a portion of the first and the second electrodes, the microchannel being defined by the surface of the support and the spacer.

When a first liquid is contacted with the first electrode, and a second liquid is contacted with the second electrode, a multistream laminar flow is established between the first and the second liquids, and a current density of at least 0.1 mA/cm^2 is produced.

5   The presently preferred embodiments described herein may possess one or more advantages relative to other devices and methods, which can include but are but not limited to: reduced cost; increased cell lifetime; reduced internal resistance of the cell; reduction or elimination of methanol crossover or fouling of the cathode; ability to recycle left-over methanol that

10   crosses over into the oxidant stream back into the fuel stream; ability to increase reaction kinetics proportionally with temperature and/or pressure without compromising the integrity of a membrane; and ability to fabricate a highly efficient, inexpensive, and lightweight cell.

BRIEF DESCRIPTION OF THE DRAWINGS

15   FIG. 1 shows a cross-sectional schematic illustration of a polymer electrolyte fuel cell.

FIG. 2 shows a cross-sectional schematic illustration of a direct methanol fuel cell.

FIG. 3 shows a schematic illustration of modes of fluid flow.

20   FIG. 4 shows a schematic illustration of the relationship between input stream geometry and mode of fluid flow.

FIG. 5 shows a schematic illustration of the relationship between microfluidic flow channel geometry and mode of fluid flow.

FIG. 6 shows a schematic illustration of a diffusion-based micro-

25   extractor.

FIG. 7 shows a schematic illustration of a direct methanol fuel cell containing a laminar flow induced dynamic interface.

FIG. 8A shows a schematic illustration of side-by-side microfluidic channel configuration and 8B shows a face-to-face microfluidic channel

30   configuration.

FIG. 9 shows a perspective view of a laminar flow fuel cell in accordance with the present invention.

FIG. 10 shows an exploded perspective view of the fuel cell shown in FIG. 9.

5   FIG. 11 shows a plot of current vs. voltage for a copper-zinc laminar flow fuel cell.

FIG. 12 shows a plot of current vs. voltage for a platinum-platinum laminar flow fuel cell.

FIG. 13A shows the top view of a laminar flow cell with face-to-face

10   electrodes, and 13B its cross-section.

FIG. 14 shows a plot of potential vs. current density plot for a laminar fuel cell with a ferrous sulfate and potassium permanganate fuel-oxidant combination.

Fig. 15 shows a power density to potential plot for a laminar fuel cell

15   with a ferrous sulfate and potassium permanganate fuel-oxidant combination.

FIG. 16 shows a plot of potential vs. current density plot for a laminar fuel cell with a formic acid and oxygen saturated aqueous sulfuric acid fuel-oxidant combination.

Fig. 17 shows a power density to potential plot for a laminar fuel cell

20   with a formic acid and oxygen saturated aqueous sulfuric acid fuel-oxidant combination.

FIG. 18 shows a plot of potential vs. current density plot for a laminar fuel cell with a formic acid and potassium permanganate fuel-oxidant combination.

25   Fig. 19 shows a power density to potential plot for a laminar fuel cell with a formic acid and potassium permanganate fuel-oxidant combination.

FIG. 20 shows a plot of potential vs. current density plot for a laminar fuel cell with a methanol and oxygen saturated aqueous sulfuric acid fuel-oxidant combination.

30   Fig. 21 shows a power density to potential plot for a laminar fuel cell with a methanol and oxygen saturated aqueous sulfuric acid fuel-oxidant combination.

DETAILED DESCRIPTION

A revolutionary paradigm in cell design, which solves many of the problems described above, has been discovered wherein the use of a PEM has been eliminated entirely. An electrochemical cell in accordance with the present invention does not require a membrane, and is therefore not constrained by the limitations inherent in conventional membranes. Instead, a mechanism has been developed by which ions can travel from one electrode to another without traversing a membrane, and which allows proton conduction while preventing mixing of the fuel and oxidant streams. This mechanism, described more fully herein below, involves establishing laminar flow induced dynamic conducting interfaces.

Throughout this description and in the appended claims, the phrase "electrochemical cell" is to be understood in the very general sense of any seat of electromotive force (as defined in *Fundamentals of Physics, Extended Third Edition* by David Halliday and Robert Resnick, John Wiley & Sons, New York, 1988, 662 ff.). The phrase "electrochemical cell" refers to both galvanic (i.e., voltaic) cells and electrolytic cells, and subsumes the definitions of batteries, fuel cells, photocells (photovoltaic cells), thermopiles, electric generators, electrostatic generators, solar cells, and the like. In addition, throughout this description and in the appended claims, the phrase "complementary half cell reactions" is to be understood in the very general sense of oxidation and reduction reactions occurring in an electrochemical cell.

Ideally, the structural components of a DMFC will have the following characteristics. Preferably, the membrane should (1) be resistant to harsh oxidizing/reducing environments; (2) possess mechanical toughness; (3) be resistant to high temperatures and pressures (e.g., 0-160 °C and 1-10 atm); (4) be impermeable to methanol under all operating conditions; (5) conduct protons with minimal ohmic resistance and mass transport losses; and (6) be composed of lightweight and inexpensive materials. Both the anode and cathode, preferably, should (1) exhibit high catalytic activity; (2) possess a large surface area; (3) require minimal amounts of precious metals; and (4) be

easily to fabricated. In addition, the anode should preferably show tolerance to carbon monoxide, and the cathode should preferably show tolerance to methanol if so needed. The integrated fuel cell assembly itself should preferably (1) have few moving parts; (2) require no external cooling system; (3) require no fuel reformer or purifier; (4) be composed of durable and inexpensive components; (5) be easily fabricated; (6) be easily integrated into fuel cell stacks; and (7) provide highly efficient energy conversion (i.e., at least 50%).

Heretofore, there has been no single fuel cell design that successfully incorporates all of the aforementioned attributes. However, it has now been discovered that by completely eliminating the PEM from the DMFC, and by redesigning the system to function on the microfluidic scale, one or more of these attributes can be achieved. In the absence of a PEM, a mechanism to allow proton conduction while preventing mixing of the fuel and oxidant streams is needed. Such a mechanism, described more fully herein below, can be established in microfluidic flow channels through a phenomenon known as "multistream laminar flow," whereby two liquid streams flow side-by-side in physical contact (thereby enabling proton conduction), without mixing and in the complete absence of a physical barrier or membrane. The two liquids can be miscible or immiscible. Obviation of a physical membrane for stream segregation and proton transport from a fuel cell significantly decreases manufacturing costs and increases the efficiency and versatility of the cell.

As shown in FIG. 3, fluid flow can be categorized into two regimes: laminar flow and turbulent flow. In steady or laminar flow (FIG. 3), the velocity of the fluid at a given point does not change with time (i.e., there are well-defined stream lines). In turbulent flow the velocity of the fluid at a given point does change with time. While both laminar and turbulent flow occur in natural systems (e.g., in the circulatory system), turbulent flow generally predominates on the macroscale. In contrast, laminar flow is generally the norm on the microfluidic scale.

An indicator of the state of a flow stream for a fluid under flow can be expressed as a dimensionless quantity known as the Reynolds number (Re). The Reynolds number is defined as the ratio of inertial forces to viscous forces, and can be expressed as:

$$Re = \rho v L / \mu$$

where L is the characteristic length in meters, ρ is the density of the fluid in grams/cm^3, v is the linear velocity in meters/sec , and μ is the viscosity of the fluid in grams/(sec)(cm).

There is a transitional critical value of Re for any given geometry above which flow is said to be turbulent and below which flow is said to be laminar. For typical fluidic devices, the transition from laminar to turbulent flow has been empirically determined to occur around Re = 2,300. Formulae to calculate Re for specific geometries are well known (see: *Micromachined Transducers: Sourcebook* by G. T. A. Kovacs, McGraw-Hill, Boston, 1998). In some microchannel geometries, flow is strictly laminar, reducing the mixing of two miscible streams to the low levels due to the interdiffusion of both liquids into each other. However, as shown in FIG. 4, the geometry of the input streams can greatly affect turbulence and mixing. A T-junction brings two miscible streams together in a laminar flow, which is maintained without turbulent mixing. In contrast, introducing the two streams in an arrow-type junction would produce turbulent flow and subsequent mixing.

Geometry is not the only variable that affects the degree of mixing. The residence time, or flow rates of solutions can have an impact as well. The average time for a particle to diffuse a given distance depends on the square of that distance. A diffusion time scale (T_d) can be expressed as

$$T_d = L^2 / D$$

where L is the relevant mixing length in micrometers and D is the diffusion coefficient. The rate of diffusion for a given molecule is typically determined by its size. A table of diffusion coefficients for some common molecules is shown below in Table 1 (see: J. P. Brody, and P. Yager, "Diffusion-Based Extraction in a Microfabricated Device," *Sensors and Actuators*, Jan., **1997,**

A58, no. 1, pp. 13-18). As may be seen from this Table, the proton (H^+) has the highest diffusion coefficient in water at room temperature.

Table 1

Water Soluble Molecule	Molecular Weight (AMU)	Diffusion Coefficient In Water at Room Temp ($\mu\ m^2$/sec)
H^+	1	9,000
Na^+	23	2,000
O_2	32	1,000
Glycine	75	1,000
Hemoglobin	6×10^4	70
Myosin	4×10^5	10
Tobacco Mosaic Virus	4×10^7	5

When two fluids with differing concentrations or compositions of molecules are forced to flow parallel to one another in a single channel, extraction of molecules can be accomplished on the basis of diffusion coefficient differences. For example, as shown in FIG. 6, Na^+ can be extracted from blood plasma by controlling channel dimension, flow rate, and the dwell time the two streams are in contact, thus producing a continuous micro-extractor (see: Brody reference, *vide supra*).

It has been discovered that multistream laminar flow between two miscible streams of liquid induces an ultra-thin dynamic conducting ("semi-permeable") interface (hereinafter "induced dynamic conducting interface" or "IDCI"), which wholly replaces the PEMs or salt bridges of conventional devices. The IDCI can maintain concentration gradients over considerable flow distances and residence times depending on the dissolved species and the dimensions of the flow channel.

An electrochemical cell embodying features of the present invention includes (a) a first electrode; (b) a second electrode; and (c) a channel contiguous with at least a portion of the first and the second electrodes. When a first liquid is contacted with the first electrode, a second liquid is contacted with the second electrode, and the first and the second liquids flow

through the channel, a multistream laminar flow is established between the first and the second liquids, and a current density of at least 0.1 mA/cm^2 is produced.

Flow cell designs embodying features of the present invention

5   introduce a new paradigm for electrochemical cells. A fuel cell **20** embodying features of the present invention that does not require a PEM nor is subject to several of the limitations imposed by conventional PEMs is shown in FIG. 7. In this design, both the fuel input **22** (e.g. an aqueous solution containing MeOH and a proton source) and the oxidant input **24** (e.g., a solution

10   containing dissolved oxygen or hydrogen peroxide and a proton source) are in liquid form. By pumping the two solutions into the microchannel **26**, multistream laminar flow induces a dynamic proton-conducting interface **28** that is maintained during fluid flow. If the flow rates of the two fluids are kept constant and the electrodes are properly deposited on the bottom and/or top

15   surfaces of the channel, the IDCI is established between anode **30** and cathode **32**.

A proton gradient is created between the two streams and rapid proton diffusion completes the circuit of the cell as protons are produced at anode **30** and consumed at cathode **32**. In this case, the IDCI prevents the two

20   solutions from mixing and allows rapid proton conduction by diffusion to complete the circuit.

Preferably, the liquid containing the fuel and the liquid containing the oxidant each contains a common electrolyte, which is preferably a source of protons (e.g., a Brønsted acid). A portion of these externally provided protons

25   may be consumed in the half-cell reaction occurring at the cathode. Thus, a reliance on pure diffusion for conveying protons from the fuel stream to the oxidant stream can be avoided and current densities of at least 0.1 mA/cm^2 can be achieved.

Preferably, an electrochemical cell embodying features of the present

30   invention produces current densities of at least 0.1 mA/cm^2, more preferably of at least 1 mA/cm^2, still more preferably of at least 2 mA/cm^2. A current density of 27 mA/cm^2 has been produced in accordance with presently

preferred embodiments. Although there is presently no preferred limit to the amount of current density produced by an electrochemical cell embodying features of the present invention, it is preferred that the current density produced by a cell be substantially matched to the requirements for a

5   particular application. For example, if an electrochemical cell embodying features of the present invention is to be utilized in a cellular phone requiring a current density of about 10 mA/cm^2, it is preferred that the electrochemical cell produce a current density that is at least sufficient to match this demand.

Advantages of the design shown in FIG. 7 include but are not limited to

10   the following: reduced cost due to the elimination of a PEM; increased cell lifetime due to the continual regeneration of the IDCI, which neither wears out nor fails under flow; reduced internal resistance of the cell due to the infinite thinness of the IDCI; reduction or elimination of methanol crossover or fouling of the cathode since, with proper design, diffusion occurs only downstream of

15   the cathode; ability to recycle back into the fuel stream left-over methanol that crosses over into the oxidant stream; ability to increase reaction kinetics proportionally with temperature and/or pressure without compromising the integrity of the IDCI; ability to fabricate a highly efficient, inexpensive, and lightweight cell through optimization of cell dimensions, flow rate, fuel

20   (concentration and composition), oxidant (concentration and composition) and electrodes (surface area, activity, and chemical composition).

In an optimized cell design, the methanol is completely consumed before it diffuses into the oxidant stream. This is feasible if the concentration of methanol is controlled by a methanol sensor coupled to a fuel injector or to

25   a flow rate monitor. Alternatively, a water immiscible oxidant fluid stream having a very low affinity for methanol and a high affinity for oxygen and carbon dioxide can be used in conjunction with the laminar flow-type cell shown in FIG. 7. At least one such family of fluids (viz., perfluorinated fluids such as perfluorodecalin available from F2 Chemicals Ltd., Preston, UK) has

30   been successfully used in respiration-type fluids for medicinal applications. These fluids exhibit an extremely high affinity for oxygen and extremely low affinities for methanol and water. They are chemically inert and thermally

stable. When these fluids are doped with NAFION or an alternative proton source, they become proton conducting. Thus, inasmuch as methanol is soluble in the aqueous fuel stream only, the unwanted problem of methanol crossover into the water immiscible oxidant fluid stream is reduced or

5   eliminated. Moreover, since both liquids are excellent heat exchangers, an external cooling system is not required.

Cell and electrode dimensions and electrode placement affect cell efficiency. FIG.8 shows two alternative cell designs. In FIG. 8A, the anode and cathode are positioned side-by-side, analogous to the placement shown

10   in FIG. 7. In FIG. 8B, the anode and cathode are positioned face-to-face. The optimization of cell dimensions can be achieved via computer modeling (e.g., using fluid flow modeling programs, Microsoft EXCEL software, etc.) to correlate optimum laminar flow conditions (i.e., minimum mixing) with easily fabricated channel dimensions and geometries. Critical values for the

15   Reynolds number can be calculated for an array of cell designs with respect to channel width, depth, length, flow rate, and interfacial surface area. In this manner, a channel design that provides the greatest power output and highest fuel conversion can be determined.

When appropriate electrode dimensions and placement of electrodes

20   have been determined as set forth above, the electrodes are then patterned onto a support (e.g., a soda lime or Pyrex glass slide). The electrodes may be sacrificial electrodes (i.e., consumed during the operation of the electrochemical cell) or non-sacrificial electrodes (i.e., not consumed by the operation of the electrochemical cell). In preferred embodiments, the

25   electrodes are non-sacrificial. In any event, the type of electrode used in accordance with the present invention is not limited. Any conductor with bound catalysts that either oxidize or reduce methanol or oxygen is preferred. Suitable electrodes include but are not limited to carbon electrodes, platinum electrodes, palladium electrodes, gold electrodes, conducting polymers,

30   metals, ceramics, and the like.

The electrode patterns can be produced by spray coating a glass slide and mask combination with dispersions of metallic (preferably platinum)

particles in an organic or aqueous carrier. A preferred dispersion of platinum particles in an organic carrier is the inexpensive paint product sold under the trade name LIQUID BRIGHT PLATINUM by Wale Apparatus (Hellertown, PA). The patterned slide is then baked in a high temperature oven in the

5 presence of oxygen or air to produce a thin conductive layer of pure platinum. This technique enables production of thin, high surface area, mechanically robust, low resistance platinum electrodes on glass slides. To increase the carbon monoxide tolerance of these electrodes, they can be decorated with ruthenium using chemical vapor deposition, sputtering, or a technique known

10 as spontaneous electroless deposition (see: A. Wieckowski et al. *J. Catalysis*, **2001**, in press).

Once the electrodes have been patterned on a support, the microchannel can be constructed readily from flat, inexpensive, precision starting materials as shown in FIGS. 9-10 using techniques such as those

15 described by B. Zhao, J. S. Moore, and D. J. Beebe in *Science*, **2001**, *291*, 1023-1026. Microchannel **34** can be constructed from commercially available glass slides **36** and cover slips **38**. The microchannel **34** can be sealed with an ultraviolet-based chemically resistant adhesive. A preferred ultraviolet-based chemically resistant adhesive is that sold by Norland Products, Inc.

20 (Cranberry, NJ), which is chemically resistant to most water-miscible solvents. The cell thus produced will have chemical resistance and can be employed as a single channel laminar flow DMFC.

Once a single channel laminar flow DMFC has been assembled, optimization experiments can be performed in which the efficiency of the cell

25 is evaluated with respect to concentration of methanol, concentration of proton, oxidant composition, flow rate, and temperature. Evaluation of cell performance is determined based on cell potential, current density, peak power, and power output. The single channel laminar flow DMFC is reusable, and multiple experiments can be performed with the same cell.

30 The fuel and oxidant are introduced into the flow channel with the aid of one or more pumps, preferably with the aid of one or more high-pressure liquid chromatography (HPLC) fluid pumps. For example, the flow rate of the

fuel and oxidant streams can be controlled with two HPLC pumps to enable precise variation of the flow rate from 0.01 to 10 mL/min. This approach allows for the use of large reservoirs of fuel and oxidant that can be heated to constant temperatures and maintained under inert atmosphere, air, or oxygen,

5   as needed. The effluent streams can be monitored for the presence of methanol to quantify chemical conversion, cell efficiency, and methanol crossover, by sampling the effluent stream and subjecting it to gas chromatographic analysis. In this manner, the optimized operating conditions for a single channel laminar flow DMFC can be determined.

10   It is noted that the fabrication technique described above can be readily extended to the construction of multi-channel laminar flow DMFC stacks for use in devices having increased power requirements. Likewise, the methods described above for optimizing and quantifying the efficiency of single channel laminar flow DMFCs can be used to optimize and quantify the efficiency of

15   arrayed multi-channel cell designs. The electrodes in such multi-channel cell designs can be connected in both series and parallel configurations to investigate the parameters of maximum cell voltage and current.

A single channel laminar flow DMFC can be constructed using materials with sufficient structural integrity to withstand high temperatures

20   and/or pressures. Graphite composite materials (similar to those used in DMFCs from Manhattan Scientific) or ceramic materials (similar to those used in DMFCs from Los Alamos National Laboratory) can be used in view of their light weight, mechanical integrity, high temperature stability, corrosion resistance, and low cost. In addition, a variety of fabrication techniques can

25   be used to produce the microchannel including micro-milling, micro-molding, and utilizing an Electric Discharge Machine (EDM) such as is used in the fabrication of injection molds. The electrodes can be deposited as described above, and a chemically inert gasket used to seal the cell. The gasket can be made, for example, from a fluoropolymer such as polytetrafluoroethylene sold

30   under the trade name TEFLON by DuPont (Wilmington, DE). Alternative sealing techniques such as those utilized by Manhattan Scientifics can also be employed. Optimization and quantification of the efficiency of these single

channel laminar flow DMFCs can be achieved using the techniques described above.

Although the manner of establishing and utilizing an induced dynamic conducting interface in accordance with the present invention has been described primarily in reference to a DMFC, it is emphatically noted that the concepts and principles described herein are general to all manner of electrochemical cells, including but not limited to other types of fuel cells and to batteries, photocells, and the like.

The manner in which a device embodying features of the present invention is made, and the process by which such a device is used, will be abundantly clear to one of ordinary skill in the art based upon joint consideration of both the preceding description, and the following representative procedures. It is to be understood that many variations in the presently preferred embodiments illustrated herein will be obvious to one of ordinary skill in the art, and remain within the scope of the appended claims and their equivalents.

EXAMPLES

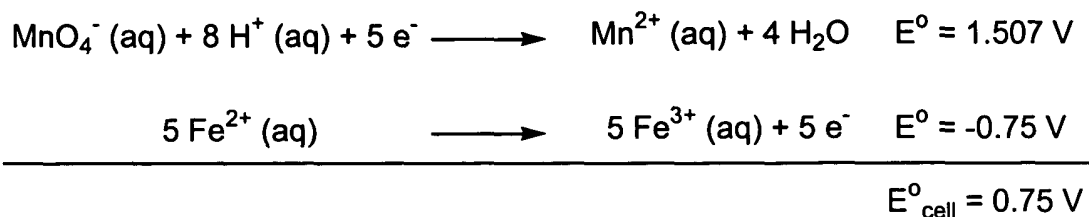### A Laminar Flow Cell Using Sacrificial Electrodes

Flat copper and zinc electrodes (*ca.* 0.125 x 20 x 3 mm) were imbedded into a block of polycarbonate by micro-machining channels and adhering the electrodes into these channels to create a flat surface. The electrodes were both of equivalent size and ran parallel to each other with a gap of approximately 5 mm there between. On top of this electrode assembly was assembled a flow channel composed of microscope coverglass as shown in Figure 11. The cell was sealed with UV glue (Norland Products Inc., Cranberry, NJ) and the input adapters were secured with commercially available epoxy (Loctite Quick Set Epoxy, Rocky Hill, CT). Once the cell was assembled, aqueous solutions of 2M copper sulphate and zinc sulphate were prepared. The zinc sulphate solution was brought into the channel first over the zinc electrode with the aid of a syringe pump (this filled the entire channel with liquid and care was take to remove all air bubbles). The copper sulphate

solution was then introduced over the copper electrode. Laminar flow was established between the electrodes and a current to voltage plot was developed as shown in FIG. 11. The flow rates of the two solutions were held constant and equal to each other (e.g., at 0.1 mL/min) in order for the induced

5   dynamic conducting interface to exist between the two electrodes. If the flow rates were different and the opposing stream touched the opposite electrode, the cell would short and produce no current. Thus, in accordance with the present electrode configurationit is preferred that the flow rates of the two solutions be similar (i.e., differ by less than about 15 percent, more preferably

10   by less than about 10 percent, and still more preferably by less than about 5 percent).

A Laminar Flow Cell Using Non-Sacrificial Electrodes

Two flat platinum electrodes (*ca.* 0.125 x 20 x 3 mm) were imbedded

15   into a block of polycarbonate by micro-machining channels and adhering the electrodes into these channels, creating a flat substrate with exposed electrode surfaces. The electrodes were both of equivalent size and ran parallel to each other with a gap of approximately 5 mm. On top of this electrode assembly was assembled a flow channel composed of double stick

20   tape and a microscope coverglass as shown in Figure 11. The cell was sealed and the input adapters were secured with commercially available epoxy (Loctite Quick Set Epoxy, Rocky Hill, CT). Next, solutions of iron (II) chloride in 10% H_2SO_4 (0.6M) and potassium permanganate in 10% H_2SO_4 (0.076M) were prepared. The iron solution was brought into the channel first

25   over the platinum electrodes with the aid of a syringe pump (this filled the entire channel with liquid and care was take to remove all air bubbles). The permanganate solution was then introduced and laminar flow was visibly established between the electrodes. The flow rates of the two solutions were held constant and equal to each other in order for the induced dynamic

30   conducting interface to exist between the two electrodes. Current flow (I) and cell potential (V) were measured with the aid of a variable resistor and potentiometer. A current to voltage plot was then developed as shown in

Figure 12, thus confirming the functioning of the device as an electrochemical cell. The flow rate was held at 0.05 mL/min and the reproducibility was good. The power plot for this data can also be seen in Figure 12. The electrochemical half reactions for the cell are as follows:

$$MnO_4^- \text{ (aq)} + 8\,H^+ \text{ (aq)} + 5\,e^- \longrightarrow Mn^{2+} \text{ (aq)} + 4\,H_2O \quad E^o = 1.507 \text{ V}$$

$$5\,Fe^{2+} \text{ (aq)} \longrightarrow 5\,Fe^{3+} \text{ (aq)} + 5\,e^- \quad E^o = -0.75 \text{ V}$$

$$E^o_{cell} = 0.75 \text{ V}$$

This particular chemistry was chosen to demonstrate the feasibility of a reaction in which all products and reactants remained in solution and utilized a common electrolyte. Since the electrodes are not involved in the reaction, their lifetimes are very long and the cell will continue to operate as long as oxidant and reductant are provided. The IDCI has an infinite lifetime because it is constantly being regenerated under flow. With this particular reaction, the dark purple permanganate solution becomes colorless at the cathode under high current conditions providing a visible means of measuring current flow. Should the effluent stream be purple, it indicates that oxidant has not been completely consumed. The color change occurs only at the cathode surface (not at the interface), further indicating true laminar flow with ion conductivity. This technology can be transferred directly to applications involving DMFCs.

A Laminar Flow Fuel Cell with Face-to-Face Electrodes

As seen in Figures 13 A and 13 B, the fuel cell system **1301** has the anode and cathode electrodes in a face-to-face orientation similar to Figure 8B. Using a very similar fabrication scheme as described below, the side-by-side orientation of the cathode and anode electrodes as shown in Figure 8A may also be obtained.

The fuel cell system **1301** includes multiple parts that are stacked in layers. In Figure 13 a schematic top view and a cross sectional view is given

of such a stacked layer assembly, wherein the fuel stream **1302** and oxidant stream **1304** will convene at a Y-shaped junction and continue to flow laminarly in parallel in the common fluidic channel **1306** in which the catalyst covered electrodes **1308** cover part of the walls.

5   The central support layer **1300** that carries the outline of the fluidic channel **1306** and supports the catalyst covered anode and cathode electrodes **1308** with their leads **1310** may be fabricated according to the following procedure. First, a negative of the channel shape, a master, is obtained in thick photoresist (SU-8 series, Microchem, Newton, MA) via

10   standard photolithographic techniques using transparency films as the mask. This master is replicated into an elastomeric mold, typically a silicone rubber (poly(dimethylsiloxane) (PDMS) or SILGARD™ 184, Dow Corning, Midland, MI), to obtain a positive relief structure of the fluidic channel **1306** (for a detailed description of this type of procedure see Duffy et al., Anal. Chem.

15   (1998) 70, pp. 4974-4984).

The mold is replicated to obtain the desired central support layer. For example, a liquid UV-curable polyurethane adhesive (Norland Optical Adhesive no. 81, Norland Products, Cranbury, NJ) is applied and spread evenly over the elastomeric mold, then a flat layer of the elastomeric material

20   is applied and clamped on top (i) to level the liquid adhesive, and (ii) to ensure that the top layer touches the top of the positive relief fluidic channel **1306**. This clamped assembly is then treated with UV light according to the manufacturer's instructions. Finally, the elastomeric top layer and the positive-relief elastomeric mold are peeled away to yield a freestanding central support

25   structure (0.5-3 mm in thickness) carrying the outlines (sidewalls) of the Y-shaped fluidic channel **1306** system.

Shadow evaporation of metals (for example, via an ATC 2000 sputtering system, AJA International Inc, North Scituate, MA) is used to apply the anode and cathode electrodes **1308** in the appropriate shapes to the

30   central support layer. Typically, chromium (usually 2-50 nm) is applied as an adhesion layer, followed by gold (usually 50-1500 nm) as the seed layer for consecutive electrodeposition of the catalyst, for example Platinum Black

plated on gold on each electrode separately at 2.6 V with a current density of about 10 mA/cm^2 for 3 minutes.

In the fuel cell system described herein both the anode and cathode consist of electrodeposited Platinum Black. Similar procedures may be used to apply other metals or combinations thereof.

The central support layer **1300** carrying the electrodes **1308** is clamped between two gasket layers **1314** (typically 1-10 mm in thickness) that form the top and the bottom wall of the fluidic channel **1306** embedded in the central support structure **1300**. These two gasket layers **1314** are shaped for easy access to the leads **1310** that are connected to the electrodes **1308**. Typically, slabs of a silicone elastomer (for example PDMS) are used as gaskets. Other materials including glass, PLEXIGLAS™, other gasket materials (for example, rubber) or a combination of any of such materials could be used as well.

To guide the fuel and oxidant into the Y-shaped channel system and to guide the waste stream out of the channel, fluidic tubing is placed in the gaskets. Typically, holes are punched exactly at the three ends **1320** of the Y-shaped channel design. If the gasket material is elastomeric (for example, PDMS) the tubes may be kept in place by a pressure-fit mechanism.

To provide rigidity and robustness to the layered system, more rigid top and bottom capping layers **1322** may be applied, such as 2 mm–thick PLEXIGLAS™. The now five layer assembly is kept together using clamps such as standard paper binding clips.

The procedure described above was used to manufacture a laminar flow cell with a channel 3.0 cm long, 1.0 mm high, and 1.0 mm electrode-to-electrode distance. This cell was used for experimenting with the fuel-oxidant combinations reported in Table 2. All experiments were run at room temperature at a 0.5 ml/min cell flow rate. Thus, in accordance with the present electrode configuration (face to face), the flow rates of the fuel and oxidant need not be equal, as even at flow rates differing by 90% the streams cannot cross over.

Table 2

Exp.	Fuel	Oxidant	Results
A	FeSO$_4$ 0.72 M in 10% aqueous H$_2$SO$_4$	KMnO$_4$ 0.144 M in 10% aqueous H$_2$SO$_4$	Fig. 14. Load Curve Fig. 15. Power Density Curve
B	10% aqueous HCOOH	1 N aqueous H$_2$SO$_4$ saturated with O$_2$	Fig. 16. Load Curve Fig. 17. Power Density
C	10% aqueous HCOOH	KMnO$_4$ 0.144 M in 10% aqueous H$_2$SO$_4$	FIG. 18. Load Curve Fig. 19. Power Density Curve
D	MeOH 1 M in water	1 N aqueous H$_2$SO$_4$ saturated with O$_2$	FIG. 20. Load Curve Fig. 21. Power Density Curve

Saturated oxygen solutions were obtained by bubbling oxygen gas (99.99%, S.J. Smith Welding Supply) through an aqueous solution of 1-50% H$_2$SO$_4$ at 298 K for at least 15 minutes. Oxygen solutions may also be prepared by bubbling oxygen or air in aqueous emulsions of fluorinated solvents as described in "Emulsions for Fuel Cells", filed June 27, 2003, inventors Larry J. Markoski et al., U.S. Patent Application Serial No. _____, Attorney Docket No. 09800240-0048, hereby incorporated by reference in its entirety. For example, an oxygen solution may be obtained by bubbling oxygen gas or air in an emulsion made by emulsifying 10 mL of perfluorodecaline (PFD) in 20 mL of 0.5 M sulfuric acid with an amount of ZONYL® FS-62 equivalent to 1% of the total weight of the emulsion.

Other examples of oxidants are solutions of ozone, hydrogen peroxide, permanganate salts, manganese oxide, fluorine, chlorine, bromine, and iodine. Other examples of fuels are solutions of ethanol, propanol, formaldehyde, ferrous chloride, and sulfur.

Current flows (I) and cell potentials (V) were measured with the aid of either a variable resistor, a potentiostat or a multimeter. The Load Curves and Power Density plots were then developed as shown in Figures 14, 15, 16, and 17, thus confirming the functioning of the device as an electrochemical cell.

The laminar flow induced interface technology described herein is applicable to numerous cells systems including but not limited to batteries, fuel cells, and photoelectric cells. It is contemplated that this technology will be especially useful in portable and mobile fuel cell systems, such as in cellular phones, laptop computers, DVD players, televisions, palm pilots, calculators, pagers, hand-held video games, remote controls, tape cassettes, CD players, AM and FM radios, audio recorders, video recorders, cameras, digital cameras, navigation systems, wristwatches, and the like. It is also contemplated that this technology will also be useful in automotive and aviation systems, including systems used in aerospace vehicles and the like.

Throughout this description and in the appended claims, it is to be understood that elements referred to in the singular (e.g., a microchannel, a fuel cell, a spacer, a fuel input, an oxidant input, and the like), refer to one or a plurality of such elements, regardless of the tense employed.

Obviously, numerous modifications and variations of the present invention are possible in light of the above teachings. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described herein.